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## (54) PHOTOCATALYST, ITS PRODUCTION AND PRODUCTION OF HYDROGEN USING THE CATALYST

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a photocatalyst with high activity comprising a laminar composite compd. having a uniform compsn. and structure, and to provide a producing method of this photocatalyst.

SOLUTION: This photocatalyst is produced by the following method. A compd. of 4A group element, ligands, a compd. of alkali metal elements and a compd. of rare earth elements are mixed in a solvents, and the mixture is heated and stirred from room temp. to 500 K to allow esterification reaction to proceed to gelate. The product is further heated at  $\leq 650$  K to remove the excess solvent and/or org. component, then heat treated at 600 to 800 K, and pulverized to produce a precursor powder. The powder is heat treated at 773 to 1300 K to produce a powder of a laminar compd. comprising alkali metal elements and 5A group elements. Then one or more kinds elected from Ni, Pt, Ir, Ru and oxides of these are deposited by 0.1 to

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## CLAIMS

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### [Claim(s)]

[Claim 1] In the approach of manufacturing the photocatalyst which makes the stratified compound which consists of alkali metals, rare earth elements, and a 4A group element coming to support more than a kind chosen from the group which consists of nickel, Pt, Ir, Ru, and those oxides (1) It is (a) to the solvent more than a kind chosen from the group which consists of water, a hydrogen peroxide, monohydric alcohol, and polyhydric alcohol. The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of 4A group element, (b) The ligand more than a kind chosen from the group which consists of a carboxylic acid, an acetylacetone, diamines, and pyridines, (c) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of alkali metals, (d) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of rare earth elements is mixed. (2) Stir heating the obtained solution to room temperature - 500 K, advance an esterification reaction, and it is made to gel. (3) Heat the obtained gel below by 650 K, and a superfluous solvent and/or a superfluous organic component are removed. (4) Grind and precursor powder is generated, after heat-treating by 600 - 800 K. (5) Said precursor powder is heat-treated by 773 - 1300K. Alkali metals, The powder of the stratified compound which consists of rare earth elements and a 4A group element is generated, and it is (6). Approach characterized by carrying out support more than of a kind chosen from the group which becomes the powder of said stratified compound from nickel, Pt, Ir, Ru, and those oxides 0.1 to 5% of the weight (metallic element conversion).

[Claim 2] It is the approach characterized by choosing said alkali metals from the group which consists of Li, Na, K, Rb, and Cs in the manufacture approach according to claim 1, choosing said 4A group element from the group which consists of Ti, Zr, and Hf, and choosing said rare earth elements from the group which consists of La, Ce, Pr, Nd, and Dy.

[Claim 3] It is the approach characterized by choosing said monohydric alcohol from the group which consists of a methanol, ethanol, isopropanol, and a butanol in the manufacture approach according to claim 1 or 2, and choosing said polyhydric alcohol from the group which consists of ethylene glycol, propylene glycol, and a butylene glycol.

[Claim 4] It is the approach which the alkoxide of said 4A group element is chosen from the group which consists of a methoxide, ethoxide, propoxide, isopropoxide, and n-butoxide in the manufacture approach according to claim 1 to 3, and the inorganic-acid salts of said 4A group element are a chloride and/or a sulfate, and is characterized by the organic-acid salts of said 4A group element being an oxalate and/or acetate.

[Claim 5] It is the approach characterized by choosing said carboxylic acid from the group which consists of a citric acid, a malic acid, a tartaric acid, a lactic acid, a glycolic acid, tricarballylic acid, a succinic acid, oxalic acid, and an acetic acid in the manufacture approach according to claim 1 to 4, and choosing said diamines from the group which consists of ethylenediamine, ethylenediaminetetraacetic acid, 1,2-propanediamine, and 1,3-propanediamine.

[Claim 6] It is the approach characterized by \*\*\*\*\* whose organic-acid salts of said alkali metals the alkoxide of said alkali metals is chosen from the group which consists of a methoxide, ethoxide, propoxide, isopropoxide, and n-butoxide in the manufacture approach according to claim 1 to 5, the inorganic-acid salt of said alkali metals is chosen from the group which consists of a carbonate, a chloride, and a nitrate, and are an oxalate and/or acetate.

[Claim 7] In the photocatalyst which makes it come 0.1 to 5% of the weight to support more than a kind chosen from the group which becomes the stratified compound which consists of alkali metals, rare earth elements, and a 4A group element from nickel, Pt, Ir, Ru, and those oxides The stratified compound which consists of said alkali metals, rare earth elements, and a 4A group element is (1). Water, It is (a) to the solvent more than a kind chosen from the group which consists of a hydrogen peroxide, monohydric alcohol, and polyhydric alcohol. The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of 4A group element, (b) The ligand more than a kind chosen from the group which consists of a carboxylic acid, an acetylacetone, diamines, and pyridines, (c) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of alkali metals, (d) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of rare earth elements is mixed. (2) Stir heating the obtained solution to room temperature - 500 K, advance an esterification reaction, and it is made to gel. (3) Heat the obtained gel below by 650 K, and a superfluous solvent and/or a superfluous organic component are removed. (4) After heat-treating by 600 - 800 K, it grinds and precursor powder is generated, and it is (5). Photocatalyst characterized by heat-treating said precursor powder by 773 -1300K, and being manufactured.

[Claim 8] In the approach of manufacturing hydrogen from a water solution using a photocatalyst according to claim 7, it is the manufacture approach of the hydrogen characterized by pH of said water solution being five or more.

[Claim 9] In the hydrogen manufacture approach according to claim 8, said water solution is the manufacture approach of the hydrogen characterized by being pure water or the hydroxide water solution of alkali metals.

[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a suitable photocatalyst to manufacture hydrogen and its manufacture approach by disassembling water using light energy.

[0002]

[Description of the Prior Art] By photodissociating water in recent years, using a semi-conductor as an electrode, the method of manufacturing hydrogen is discovered (NATURE, 238, pp.37 (1972)), and it is proposed as one of the conversion approaches of important light energy. The hydrogen and oxygen whose stratified compound K4 Nb 6O17 which supported the nickel oxide also in the photocatalyst used for those approaches is a product hardly check advance of a moisture solution reaction. The advantage that reaction yield is high It has (K.Domen, A.Kudo, A.Shinozuka, A.Tanaka, K.Maruya and T.Onishi, J.Chem.Soc.Chem.Commun., and pp.359 (1994)).

[0003] However, the yield of the conventional photocatalyst must continue amelioration further towards utilization rather than still is enough. For example, the solid phase technique which mixes niobium oxide and potassium carbonate by the predetermined mole ratio, and is calcinated by 1100-1300-degree C high temperature as the manufacture approach of K4 Nb 6O17 is known (JP,61-197033,A). However, in a solid phase technique, a reaction has the problem that it is not perfect and the unreacted particle of niobium oxide and potassium carbonate remains. In order for niobium oxide and potassium carbonate to react and for 6OK4 Nb17 composition to advance, K component and Nb component diffuse the inside of a solid-state, and it must contact mutually. In order to enlarge this diffusion rate, it is necessary to repeat heat treatment in an elevated temperature. However, heat treatment in an elevated temperature promotes grain growth, and in order to reduce remarkably the specific surface area of 6OK4 Nb17 powder obtained, sufficient catalyst property is not acquired. It is difficult to produce K4 Nb 6O17 which heat treatment in an elevated temperature causes evaporation of a component, and moreover has a uniform presentation and a uniform organization finally. Moreover, when these stratified conjugated compounds containing alkali metals are used as a photocatalyst, exchange with alkali metals and a hydrogen ion takes place in pure water, and there is a problem that a catalyst property falls.

[0004] In view of such a situation, the photocatalyst which has higher activity, especially surface area are large, and the method of manufacturing the stratified conjugated compound which has a homogeneity organization is searched for. When the conjugated compound of the shape of a layer which consists of the alkali metals, 4A group element, and rare earth elements of K2 La2 Ti3 O10 grade promising especially as a photocatalyst is created by the conventional solid phase technique, sufficient photocatalyst activity is not acquired but the further amelioration is called for.

[0005] therefore, the purpose of this invention solves the fault of the conventional manufacture approach, and consists of a stratified conjugated compound which has uniform presentation and organization -- high -- it is offering the approach of manufacturing activity photocatalyst and it.

[0006]

[Means for Solving the Problem] An example is taken by the above-mentioned technical problem. Wholeheartedly as a result of research this invention person It is made to distribute in a solution by using 4A group element and alkali metals as a stable complex. By polymer-izing the perimeter of the complex of this 4A group element and alkali metals by the polymerization reaction, forming a uniform

polymer complex, and generating a stratified conjugated compound by the pyrolysis of this polymer complex. If it discovers that the obtained stratified conjugated compound has a uniform presentation and a uniform organization, and high surface area and this stratified conjugated compound is made to support nickel, Pt, Ir, Ru, or those oxides while being able to manufacture a stratified conjugated compound at low temperature. It discovered that the photocatalyst which has high photocatalyst activity was obtained, and this invention was completed.

[0007] The approach of this invention more than a kind chosen from the group which consists of nickel, Pt, Ir, Ru, and those oxides. Namely, alkali metals, It is the approach of manufacturing the photocatalyst make the stratified compound which consists of rare earth elements and a 4A group element coming to support. (1) It is (a) to the solvent more than a kind chosen from the group which consists of water, a hydrogen peroxide, monohydric alcohol, and polyhydric alcohol. The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of 4A group element, (b) The ligand more than a kind chosen from the group which consists of a carboxylic acid, an acetylacetone, diamines, and pyridines, (c) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of alkali metals, (d) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of rare earth elements is mixed. (2) Stir heating the obtained solution to room temperature - 500 K, advance an esterification reaction, and it is made to gel. (3) Heat the obtained gel below by 650 K, and a superfluous solvent and/or a superfluous organic component are removed. (4) Grind and precursor powder is generated, after heat-treating by 600 - 800 K. (5) Said precursor powder is heat-treated by 773 - 1300K. Alkali metals, The powder of the stratified compound which consists of rare earth elements and a 4A group element is generated, and it is (6). It is characterized by carrying out support more than of a kind chosen from the group which becomes the powder of said stratified compound from nickel, Pt, Ir, Ru, and those oxides 0.1 to 5% of the weight (metallic element conversion).

[0008] The photocatalyst of this invention to the stratified compound which consists of alkali metals, rare earth elements, and a 4A group element. Moreover, nickel, It makes it come 0.1 to 5% of the weight to support more than a kind chosen from the group which consists of Pt, Ir, Ru, and those oxides. The stratified compound which consists of said alkali metals, rare earth elements, and a 4A group element is (1). Water, It is (a) to the solvent more than a kind chosen from the group which consists of a hydrogen peroxide, monohydric alcohol, and polyhydric alcohol. The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of 4A group element, (b) The ligand more than a kind chosen from the group which consists of a carboxylic acid, an acetylacetone, diamines, and pyridines, (c) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of alkali metals, (d) The compound more than a kind chosen from the group which consists of the alkoxide, organic-acid salt, and inorganic-acid salt of rare earth elements is mixed. (2) Stir heating the obtained solution to room temperature - 500 K, advance an esterification reaction, and it is made to gel. (3) Heat the obtained gel below by 650 K, and a superfluous solvent and/or a superfluous organic component are removed. (4) After heat-treating by 600 - 800 K, it grinds and precursor powder is generated, and it is (5). It is characterized by heat-treating said precursor powder by 773 - 1300K, and being manufactured.

[0009] Furthermore, the approach of this invention of manufacturing hydrogen from a water solution using the above-mentioned photocatalyst is characterized by pH of said water solution being five or more.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[1] Raw material (a) The compound 4A group element of 4A group element is chosen from Ti, Zr, and Hf. Especially Ti is desirable especially. More than a kind chosen from the group which consists of an alkoxide, an organic-acid salt, and an inorganic-acid salt as a compound of 4A group element is used. It is desirable for it to be chosen out of the group which consists of a methoxide, ethoxide, propoxide, isopropoxide, and n-butoxide as an alkoxide of 4A group element, and to use titanium tetraisopropoxide, zirconium tetra-propoxide, titanium tetra-ethoxide, etc. A chloride, a sulfate, etc. are mentioned as an inorganic-acid salt of 4A group element. In it, it is desirable to use chlorides, such as a titanium chloride, a zirconium chloride, and a chlorination hafnium. It is desirable for an oxalate and acetate to be

mentioned and to use oxalic acid titanium, an acetic-acid zirconium, etc. especially as an organic-acid salt of 4A group element.

[0011] (b) Use more than a kind chosen from the group which consists of a carboxylic acid, an acetylacetone, diamines, pyridines, and a bipyridine as a ligand ligand. Titanium and the stable complex of barium can be made to form by adding a ligand. As a carboxylic acid, it is desirable to use carboxylic acids, such as alpha-hydroxycarboxylic acid, such as \*\* citric acid, a malic acid, a tartaric acid, a lactic acid, and a glycolic acid, \*\* tricarballylic acid, a succinic acid, oxalic acid, and an acetic acid, etc. As diamines, it is desirable to use ethylenediamine, ethylenediaminetetraacetic acid, 1,2-propanediamine, 1,3-propanediamine, etc. Moreover, as pyridines, it is desirable to use a pyridine, a bipyridine, etc. Especially in these ligands, a citric acid is desirable.

[0012] (c) The compound alkali metals of alkali metals are chosen from the group which consists of Li, Na, K, Rb, and Cs. More than a kind chosen from the group which consists of an alkoxide, an organic-acid salt, and an inorganic-acid salt as an alkali-metals compound is used. It is desirable for it to be chosen out of the group which consists of a methoxide, ethoxide, propoxide, isopropoxide, and n-butoxide as an alkoxide of alkali metals, and to use a lithium methoxide, sodium methoxide, etc. Moreover, as an inorganic-acid salt of alkali metals, a carbonate, a chloride, a nitrate, etc. are mentioned and especially carbonates especially, such as a lithium carbonate, a sodium carbonate, potassium carbonate, a carbonic acid rubidium, and cesium carbonate, are desirable. An oxalate, acetate, etc. are mentioned as an organic-acid salt of alkali metals.

[0013] (d) The compound rare earth elements of rare earth elements are chosen from the group which consists of La, Ce, Pr, Nd, and Dy. More than a kind chosen from the group which consists of an alkoxide, an organic-acid salt, and an inorganic-acid salt as a compound of rare earth elements is used. It is desirable for it to be chosen out of the group which consists of a methoxide, ethoxide, propoxide, isopropoxide, and n-butoxide as an alkoxide of rare earth elements, and to use run TANTORI propoxide etc. Moreover, as an inorganic-acid salt of rare earth elements, a carbonate, a chloride, a nitrate, etc. are mentioned and especially nitrates especially, such as a lanthanum nitrate, are desirable. An oxalate, acetate, etc. are mentioned as an organic-acid salt of rare earth elements, and an oxalic acid lanthanum, an acetic-acid cerium, especially an acetic-acid lanthanum, etc. are especially desirable.

[0014] (e) Solvent component (a) Or (d) More than a kind chosen from the group which consists of water, a hydrogen peroxide, monohydric alcohol, and polyhydric alcohol as a solvent to add is used. As monohydric alcohol, a methanol, ethanol, isopropanol, n-butanol, i-butanol, a sec-butanol, a tert-butanol, etc. are desirable, and ethylene glycol, propylene glycol, a butylene glycol, etc. are desirable as polyhydric alcohol. Especially, ethylene glycol, especially propylene glycol, etc. are desirable.

[0015] [2] Although a potassium is mentioned as an example of titanium and alkali metals, a lanthanum is mentioned as rare earth elements as an example of the manufacture approach 4A group element of a stratified conjugated compound and the manufacture approach of stratified conjugated compound K2 La<sub>2</sub> Ti 3O<sub>10</sub> is explained, it can manufacture by the approach with the same said of the other element.

[0016] (1) Mixing and \*\*\*\*\* are (a) to a solvent first. A titanium compound and (b) A ligand and (c) A potassium compound and (d) It mixes adding and agitating a lanthanum compound. Especially the addition sequence of each component is (a) although not limited. -> (b) -> (c) -> (d) Considering as order is desirable.

[0017] The amount of solvents is 10-100 on the basis of one mol of titanium compounds. It is a mol and is 20-50 mols preferably. Equalization of a presentation of K2 La<sub>2</sub> Ti 3O<sub>10</sub> obtained as the amount of solvents is less than ten mols is difficult. Conversely, the amount of solvents is 100. A mixed solution is too thin when a mol is exceeded.

[0018] The addition of a ligand is 2-10 mols on the basis of one mol of titanium compounds, and it is 4-8 mols preferably. The stable complex of titanium is not obtained as the addition of a ligand is less than two mols. Moreover, even if the amount of ligands exceeds ten mols, the further facilitatory effect is not acquired.

[0019] The addition of a lanthanum compound is set up so that the presentation of K2 La<sub>2</sub> Ti 3O<sub>10</sub> may be acquired. on the other hand -- the addition of a potassium compound -- the amount more than stoichiometry -- desirable -- 1.5 of stoichiometry It considers as the amount beyond twice. The stratified compound of the K2 La<sub>2</sub> Ti<sub>3</sub> O<sub>10</sub> grade of a single phase cannot be obtained as the addition of alkali-metals compounds, such as a potassium, is under stoichiometry.

[0020] A transparent solution will be obtained, if each component is mixed with the above-mentioned compounding ratio and it stirs at the temperature (preferably room temperature) of 300 - 373 K for 2 to 5 hours. In this process, titanium and a potassium form a ligand and a stable complex.

[0021] (2) Stir heating an esterification reaction process, next said transparency solution to room temperature - 500 K, advance the esterification reaction of a ligand and a solvent, and make it gel. A macromolecule complex is generated by this esterification reaction. As for reaction time, considering as 3 - 20 hours is desirable.

[0022] (3) Heat especially the gel from which \*\*\*\*\* was obtained at the temperature of 500 - 600 K below 650 K, and remove a superfluous solvent and/or a superfluous organic component. In addition, desirable heating time is 2 - 5 hours.

[0023] (4) a last heat treatment process, then 600 - 800 K -- it is the temperature of 600 - 700 K preferably, and heat-treat for 2 to 5 hours, and obtain black powder as a precursor. An agate mortar etc. grinds this precursor lightly.

[0024] (5) Heat-treat the precursor powder with which post heating place science and engineering was obtained at the temperature of 773 -1300K, especially 800 -1100K, and obtain the powder of K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>. In addition, desirable heat treatment time amount is 2 - 5 hours. Thus, obtained K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> for photocatalysts has few unreacted parts, and it has a uniform presentation and a uniform organization.

[0025] [3] the manufacture approach of a photocatalyst -- support the photocatalyst active species more than a kind chosen as the stratified conjugated compound of profit \*\*\* K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> grade from the group which consists of nickel, Pt, Ir, Ru, and those oxides by well-known approaches, such as the sinking-in method and solid phase reaction. The desirable support approach is the sinking-in method. By the sinking-in method, after making it sink into K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> using the water solution of compounds, such as a chloride of photocatalyst active species, and a nitrate, it dries by 323 - 423 K for about 2 to 5 hours, and below 750 K, it is below 600 - 750 K preferably, and calcinates under a reducing atmosphere and/or an oxidizing atmosphere for 2 to 5 hours. If burning temperature exceeds 750 K, since grain growth will advance, it is not desirable.

[0026] As for the content of the catalytic activity kind in the photocatalyst of this invention, it is desirable that it is 0.1 - 5 % of the weight (metallic element reduced property), and it is desirable that it is especially 0.8 - 4 % of the weight (metallic element reduced property).

[0027] The above can manufacture K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> by the approach with the same said of the other stratified compound, although the manufacture approach of a stratified compound was explained to the example. As an example of a stratified compound, KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, RbCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>, and KSr<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> grade are mentioned.

[0028] [4] Explain below the manufacture approach of the hydrogen of this invention which used the manufacture approach above-mentioned photocatalyst of hydrogen. As a water solution to photodissociate, although pure water (ion exchange water, distilled water, etc. which omit compound addition for pH adjustment instead of the semantics which does not contain an impurity etc. are pointed out) is sufficient, it is desirable to use the water solution of an alkali compound etc. As an alkali compound, on the hydroxide of alkali metals, and a concrete target, a potassium hydroxide, a sodium hydroxide, a lithium hydroxide, etc. may be desirable, and you may be those mixture. The concentration of an alkali compound has desirable 1. in 0.1-1 mol /. Moreover, pH of a water solution is six or more preferably five or more. Exchange with a hydrogen ion stops being able to happen easily, and the alkali metals in a photocatalyst can make the high activity of a photocatalyst maintain by maintaining a water solution to alkalinity.

[0029] The photocatalyst of this invention is added in the above-mentioned water solution. The addition of the catalyst for photolyses is 0.5 - 5 mg/cm<sup>3</sup>. It is desirable and is especially 1 - 3 mg/cm<sup>3</sup>. It is desirable. Thus, by irradiating light at the water solution which added the catalyst for photolyses, water decomposes and hydrogen occurs. Below 550 nm of the wavelength of light to irradiate is desirable. Since the wavelength of sunlight is about 350-2000nm, it may irradiate sunlight in this invention.

Moreover, the temperature of a water solution has desirable 25-60 degrees C.

[0030] The photocatalyst of this invention obtained by the above approach has high activity compared with the conventional thing. Although the cause has a specific surface area of stratified conjugated compound K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> larger than before and it is thought that the unreacted component which

checks electrification separation in it is not to exist substantially About the detail of the charge transfer rate of catalytic activity kind HE, such as nickel, having increased from that the charge generating rate of K2 La2 Ti 3O10 increased, or K2 La2 Ti 3O10, it does not understand yet.

[0031]

[Example] The following concrete examples explain this invention to a detail further.

They are titanium tetraisopropoxide, a methanol, potassium carbonate, a citric acid (anhydrous), and a lanthanum nitrate (La(NO<sub>3</sub>)<sub>3</sub> and 6H<sub>2</sub>O) one by one to example 1 ethylene glycol 4:0.1 : 0.134 : 1:0.067 It blended by the mole ratio, and by mixing and stirring, the potassium and the citric-acid complex of titanium were formed, and the transparent solution was obtained. This solution was heated and stirred at 410 K, and the esterification reaction of a citric acid and ethylene glycol was advanced. Yellow foaming macromolecule-like gel was obtained about 5 hours after. After heating this gel by 550 K and removing a superfluous solvent and a superfluous organic component, it heat-treated by 630 K for 2 hours. Subsequently, the black powder-like precursor was obtained by grinding for 10 minutes with a Teflon rod. This precursor was heat-treated by 1173K for 2 hours, and 3OK2 La2 Ti10 crystal was manufactured. As a result of analyzing this product by X-ray diffraction (an X-ray-diffraction-analysis equipment MXP3VA system, Mac Saiensu-Sha make), 3OK2 La2 Ti10 crystal was checked, and the crystal structure by unreacted particles, such as potassium carbonate and titanium oxide, was not seen.

[0032] Weighing capacity was carried out and, in addition, the nickel chloride was dissolved in distilled water so that nickel might become 1% of the weight of K2 La2 Ti 3O10. The 3OK2 La2 Ti10 above-mentioned powder was added to this solution, and mixed churning was carried out. After distributing homogeneity, heating churning was carried out at 50-80 degrees C, moisture was evaporated, and the sample which hardened by drying was dried by 373 \*\* for 3 hours. And it heat-treated in air for 673 K or 3 hours, and the photocatalyst was obtained. When this catalyst was measured with the BET adsorption method, surface areas were 5m<sup>2</sup> / g.

[0033] It is pure water 1.4 in 1g of this catalyst. It added in the liter, the high-pressure mercury lamp (400W, hnu>=290 nm) was irradiated, and the quantum of the oxygen and hydrogen which are generated by the moisture solution reaction was carried out by the gas chromatograph. The mole ratio of the amount of generation of oxygen and hydrogen is about 1:2, and full disassembly of water was obtained. The yield of hydrogen and oxygen is shown in Table 1.

[0034] It is a 0.1N potassium hydroxide solution 1.4 in 1g of photocatalysts created in the example 2 example 1. It added in the liter, the high-pressure mercury lamp (400W, hnu>=290 nm) was irradiated, and the quantum of the oxygen and hydrogen which are generated by the moisture solution reaction was carried out by the gas chromatograph. The mole ratio of the amount of generation of oxygen and hydrogen is about 1:2, and full disassembly of water was obtained. The yield of hydrogen and oxygen is shown in Table 1.

[0035] After mixing potassium carbonate powder with example of comparison 1 lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), and titanium oxide (TiO<sub>2</sub>) by the mole ratio of 1:3:1, it calcinated by 1323K by the solid phase technique for 48 hours, respectively, and K2 La2 Ti 3O10 was obtained. Although formation of 3OK2 La2 Ti10 crystal was accepted as a result of analyzing by X-ray diffraction like an example 1, survival of titanium oxide and potassium carbonate was checked.

[0036] Weighing capacity was carried out and, in addition, nickel nitrate was dissolved in distilled water so that nickel might become 1% of the weight of K2 La2 Ti 3O10. The 3OK2 La2 Ti10 above-mentioned powder was added to this solution, and mixed churning was carried out. After distributing homogeneity, heating churning was carried out by 320 - 350 K, moisture was evaporated, and the sample which hardened by drying was dried by 373 K for 24 hours. and the inside of the air after carrying out reduction processing of the mixed gas (hydrogen gas/nitrogen gas = 2/98) of hydrogen and nitrogen by (flow rate 250 ml/min) and 773 K with a sink for 2 hours -- 750 K -- it heat-treated for 7 hours and the photocatalyst was obtained. When this catalyst was measured with the BET adsorption method, surface areas were 1-2m<sup>2</sup> / g.

[0037] With the same approach as an example 1, it is pure water 1.4 in 1g of this catalyst. It added in the liter, the high-pressure mercury lamp (400W, hnu>=290 nm) was irradiated, and the quantum of the oxygen and hydrogen which are generated by the moisture solution reaction was carried out by the gas chromatograph. The yield of hydrogen and oxygen is shown in Table 1.

[0038] It is a 0.1N potassium hydroxide solution 1.4 in 1g of photocatalysts created in the example 1 of

example of comparison 2 comparison. It added in the liter, the high-pressure mercury lamp (400W, hnu>=290 nm) was irradiated, and the quantum of the oxygen and hydrogen which are generated by the moisture solution reaction was carried out by the gas chromatograph. The mole ratio of the amount of generation of oxygen and hydrogen is about 1:2, and full disassembly of water was obtained. The yield of hydrogen and oxygen is shown in Table 1.

[0039] Table 1 Amount of generation of hydrogen in photolysis of water, and oxygen (unit: mumol/h)  
Example No The amount of hydrogen generation The amount example 1 of oxygen generation 1200 600  
examples 2 2400 Example 1 of 1200 comparisons 500 Example 2 of 250 comparisons 550 275 [0040]  
As shown in Table 1, even if it similarly used nickel as a catalytic activity kind, the activity of the photocatalyst of the examples 1 and 2 supported to K2 La2 Ti 3O10 of this invention was about 3 to 4 times the activity of the catalyst of the examples 1 and 2 of a comparison supported to K2 La2 Ti 3O10 manufactured by the conventional solid phase technique.

[0041]

[Effect of the Invention] As explained in full detail above, since the approach of this invention manufactures the photocatalyst which consists of the alkali metals of K2 La2 Ti3 O10 grade, rare earth elements, and a 4A group element by the complex polymerization, an unreacted component does not remain in the photocatalyst obtained, but a presentation and its organization are very uniform. Moreover, since a photocatalyst can be manufactured at low temperature, the advantage of a low manufacturing cost is acquired. Furthermore, the photocatalyst of this invention has high catalytic activity, and is suitable for the photolysis of water.

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[Translation done.]